Working Group 1
Near-Field Chemistry

- What is near-field chemistry? Issues are connected with emissions and background influences

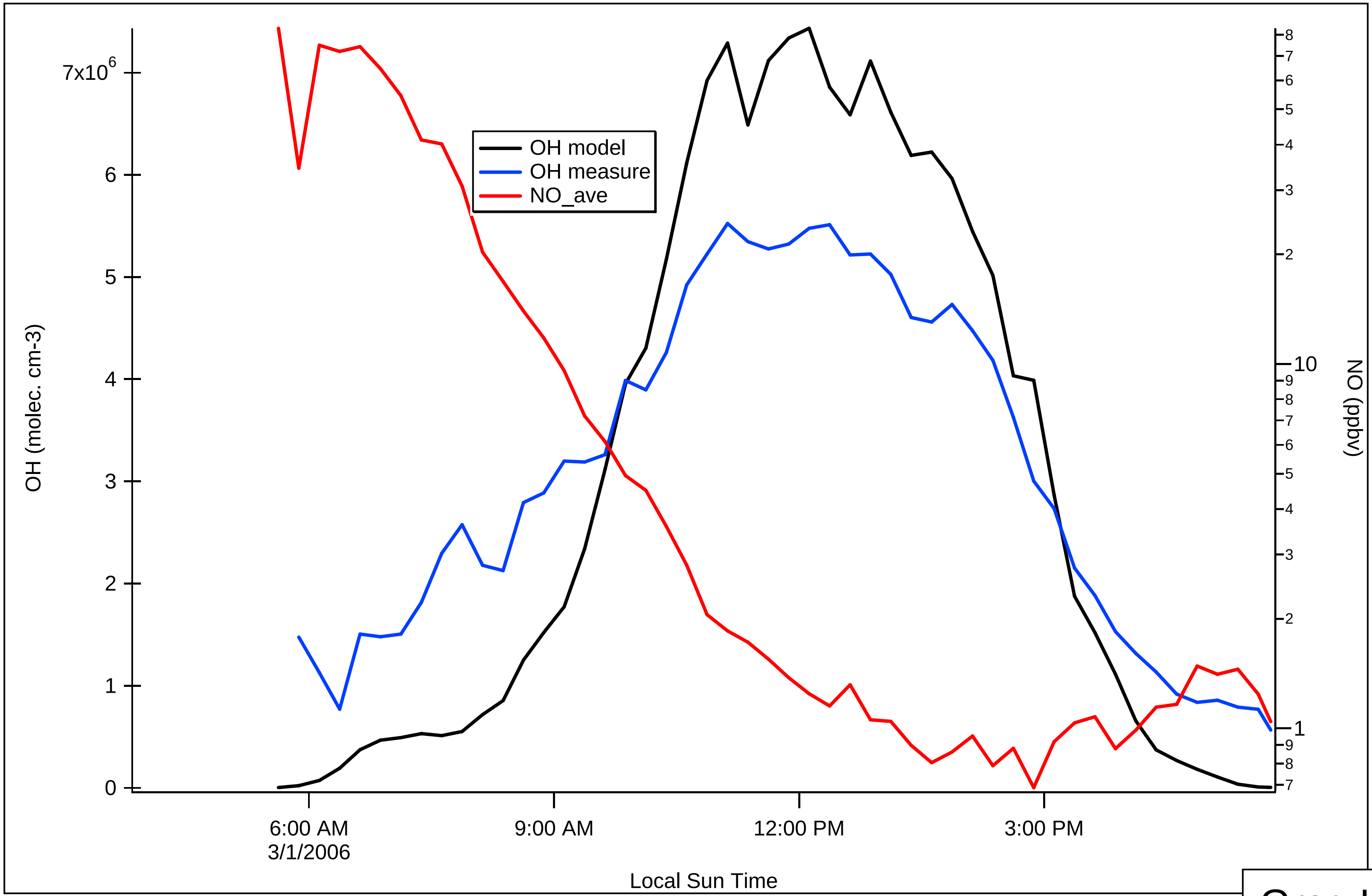
- HOx chemistry
- Formation of secondary species
- Biomass burning influences
- Regional sources

HOx Chemistry

- HO and HO_2 data from T0 and T1
- Early morning (high NOx and VOCs): measured OH >> calculated OH
- Volkamer: OH from HONO and O_3+alkenes
- Ozone production rate the highest in the early morning; lower later in the day when NOx is lower
- Transition from VOC to NOx limitation? More work needed

Data from T1

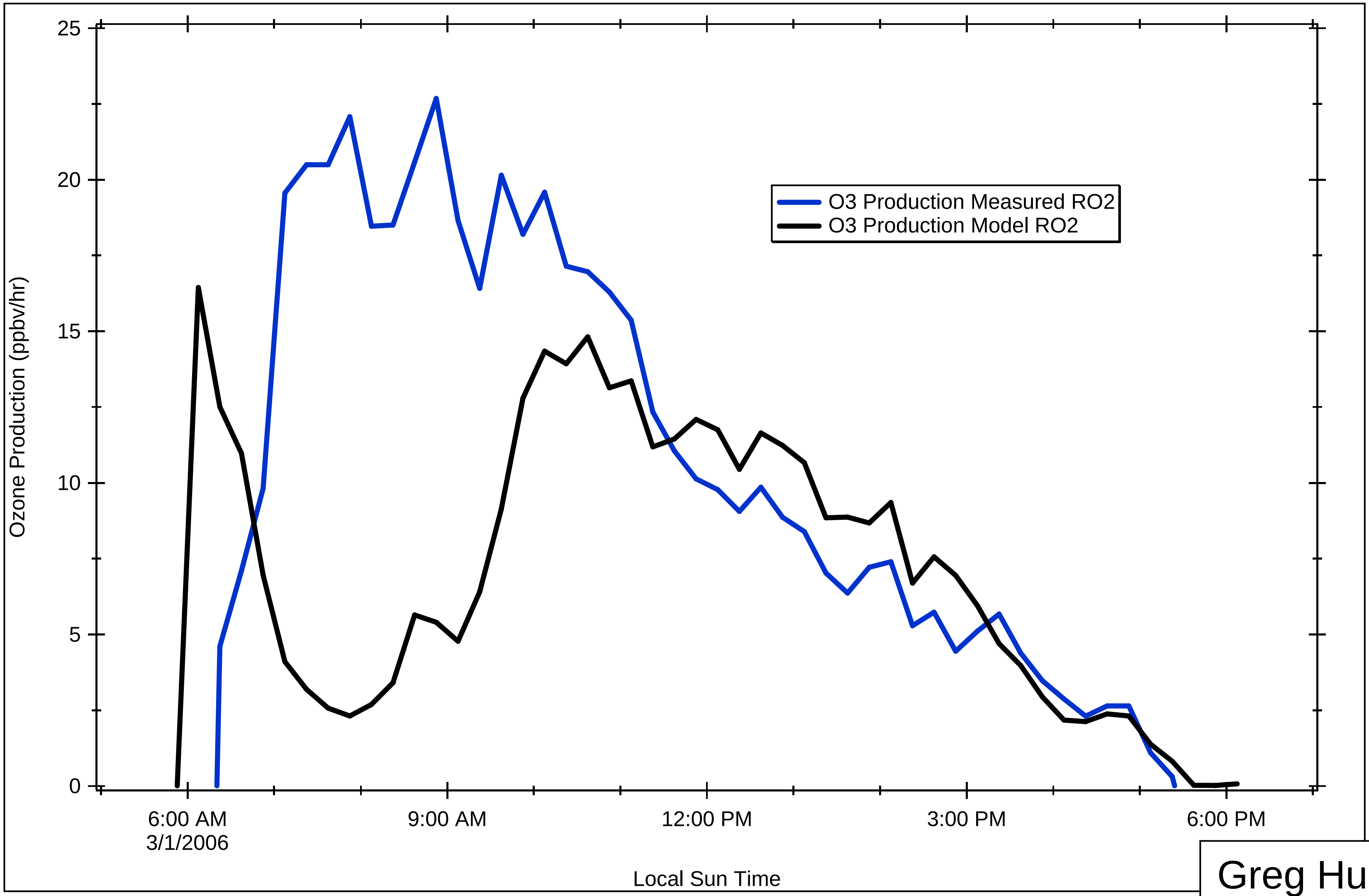
Composite OH Data



Greg Huey

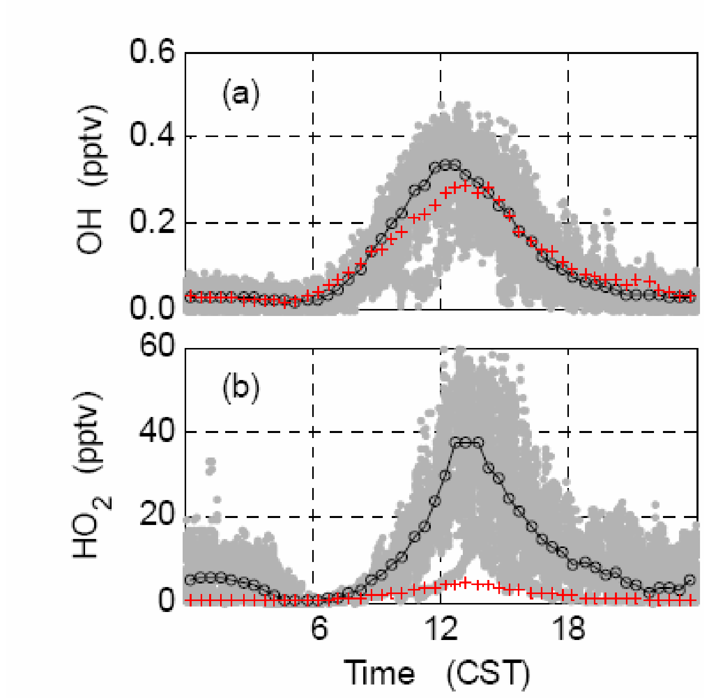
Data from T1

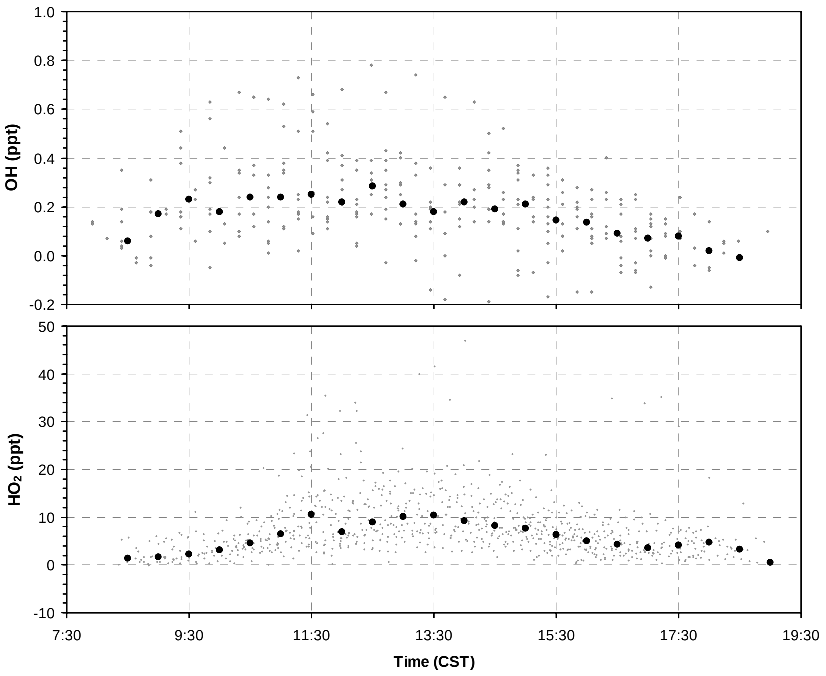
Ozone Production



Greg Huey

Diurnal profiles of OH and HO_2 MCMA-2003, 2006





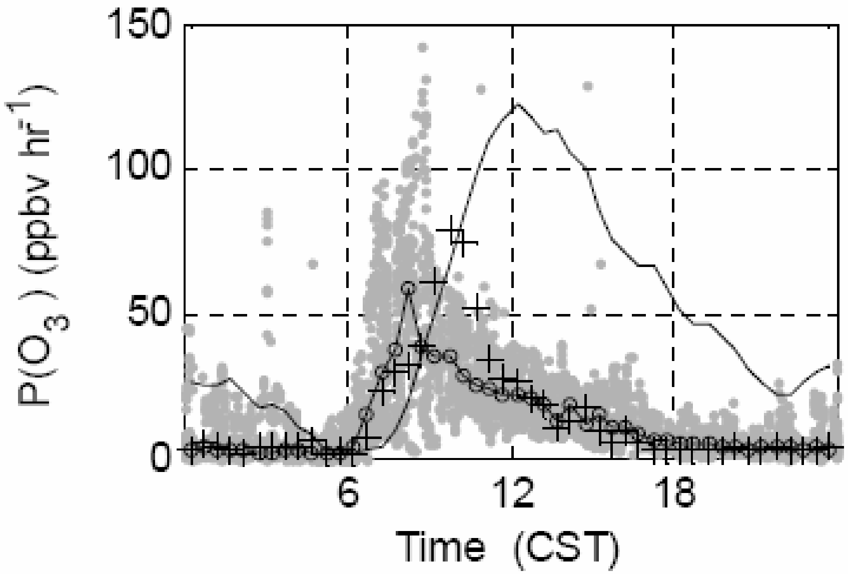
Data from T0

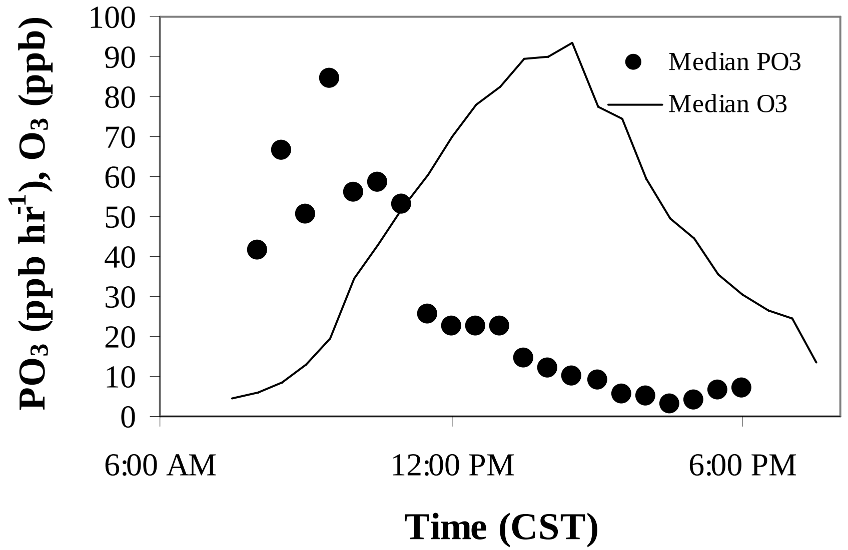
Shirley et al., *Atmos. Chem. Phys.*, **2006,** *6*, 2753

Phil Stevens

Instantaneous PO_3(HOx) 2003 and 2006

$$P_{O_3} = k_{HO_2+NO}[HO_2][NO] - k_{OH+NO_2}[OH][NO_2]$$





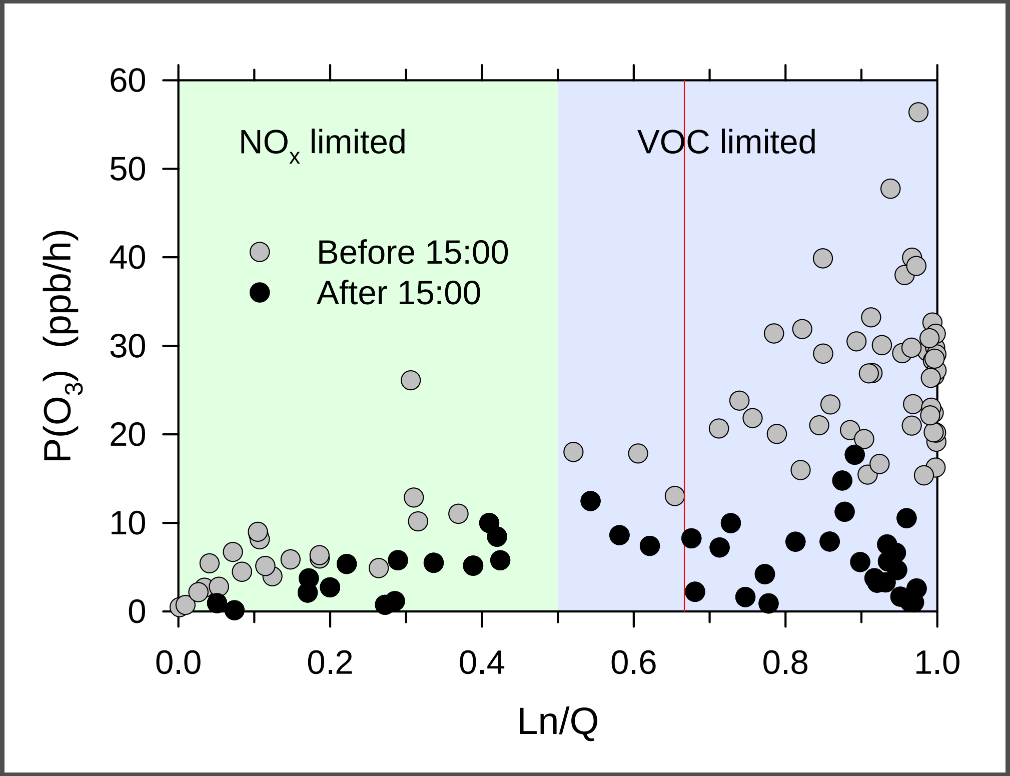
Shirley et al., *Atmos. Chem. Phys.*, **2006,** *6*, 2753

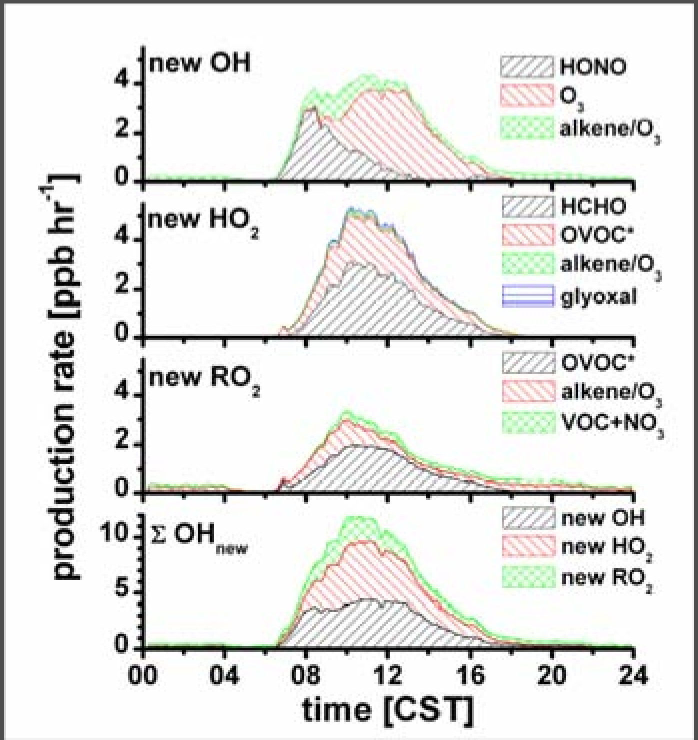
Data from T0

Phil Stevens

Highest $P(O_3)$ from VOC Limited Conditions

Data from G-1: Kleinman





$P(O_3)$ = Y ☞ Q ☞ $(VOC/NO_2)_{reactivity}$

$P(O_3)$ variability mostly due to Q

More than O_3 and HCHO for Q

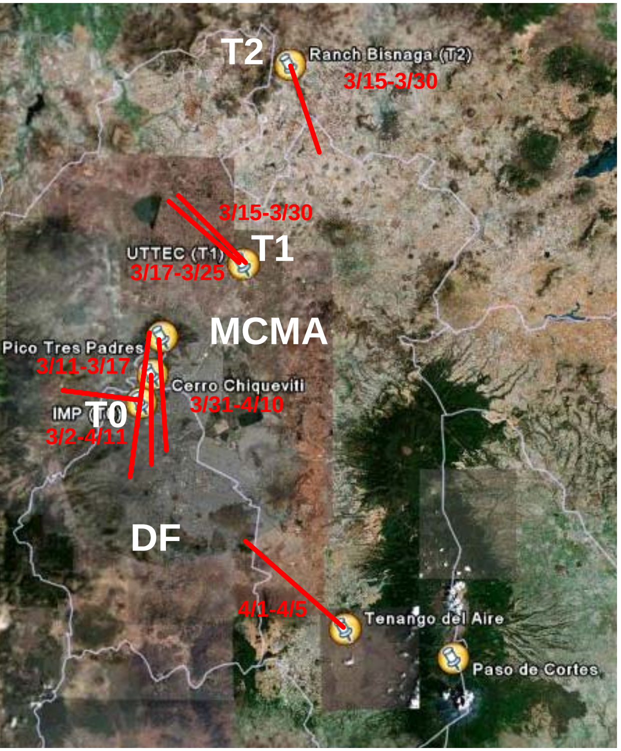
Volkamer et al., ACPD, 2007

Larry Kleinman

Measurement Results

„Alignment event“ on March 19 (wind came from the south):

Values at 7am:



	HONO VCD [cm^{-2}]	NO_2 VCD [cm^{-2}]	HONO-to-NO_2 ratio [%]	Distance from T0 [km]
T0	$1.8\cdot10^{15}$ ($\pm1.6\cdot10^{14}$)	$3.5\cdot10^{16}$ ($\pm6.1\cdot10^{14}$)	5.2 (± 0.5)	0
T1	$5.3\cdot10^{14}$ ($\pm9.4\cdot10^{13}$)	$2.8\cdot10^{15}$ ($\pm3.7\cdot10^{14}$)	19 (± 4)	30
T2	$5.1\cdot10^{14}$ ($\pm1.63\cdot10^{14}$)	$2.05\cdot10^{15}$ ($\pm4\cdot10^{14}$)	25 (± 10)	63

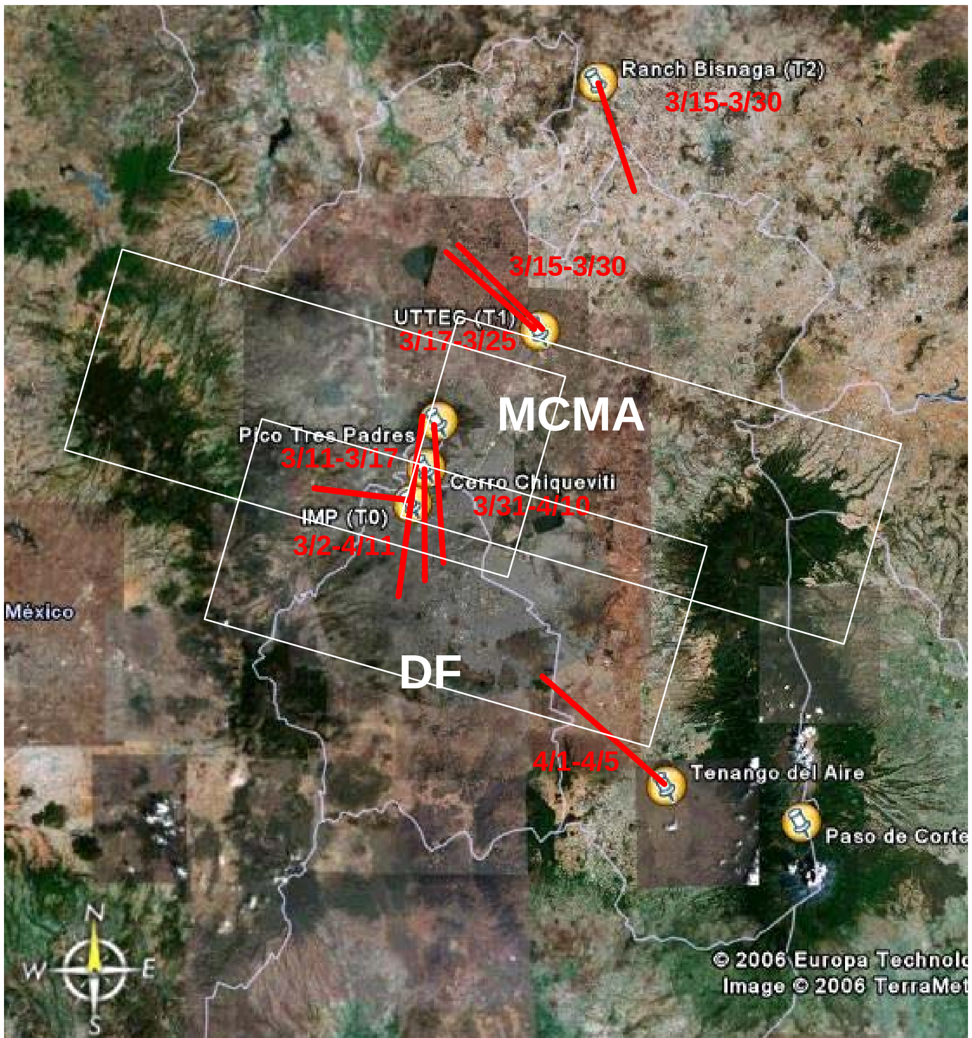
~ x3 **~ x15**

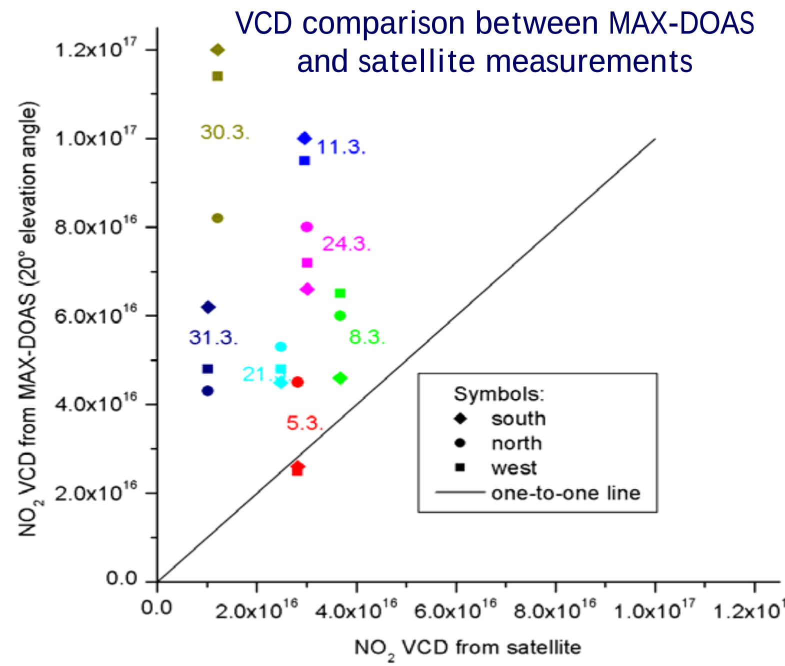
→ HONO production on surfaces

→ Relatively more HONO outside the city, why ?

→ Differences in PBL height can NOT explain this

NO_2 comparison of VCDs measured by MAX-DOAS and SCIAMACHY





Factors to consider: Spatial (temporal) overlap, radiative transfer, clouds, aerosols, albedo…

Formation of secondary species

- VOC emission ratios vs. CO (and CO2) are higher than in the U.S.
- Secondary formation of oxygenated VOCs and SOA (per CO emitted) not obviously higher than in the U.S.
- Evidence for emissions of semi-volatile organic compounds $\Rightarrow$ potential precursors of SOA

Comparison of Emissions with U.S.: Summary

Compound	OH reactivity (s^{-1} [ppmv CO]$^{-1}$)		Carbon mass (μg C m^{-3} [ppmv CO]$^{-1}$)	
	U.S.	Mex	U.S.	Mex
Alkanes	0.94 †	2.04	42 †	83
Alkenes	2.84	5.89	8.4	15
Aromatics	2.15	4.64	23	44

† for the alkanes measured during Milagro

VOC signature = dirty vehicles + additional alkanes

Data from T1: de Gouw

Data from C-130: Eric Apel

Urban Emission ratios:

ΔVOC/ΔCO (ppt/ppb)

Compare MCMA urban emission ratios w/ recent measurements in NA*

In general: oxygenates higher, low MW HCs higher, MCMA more like LA than NE

Possible reasons:

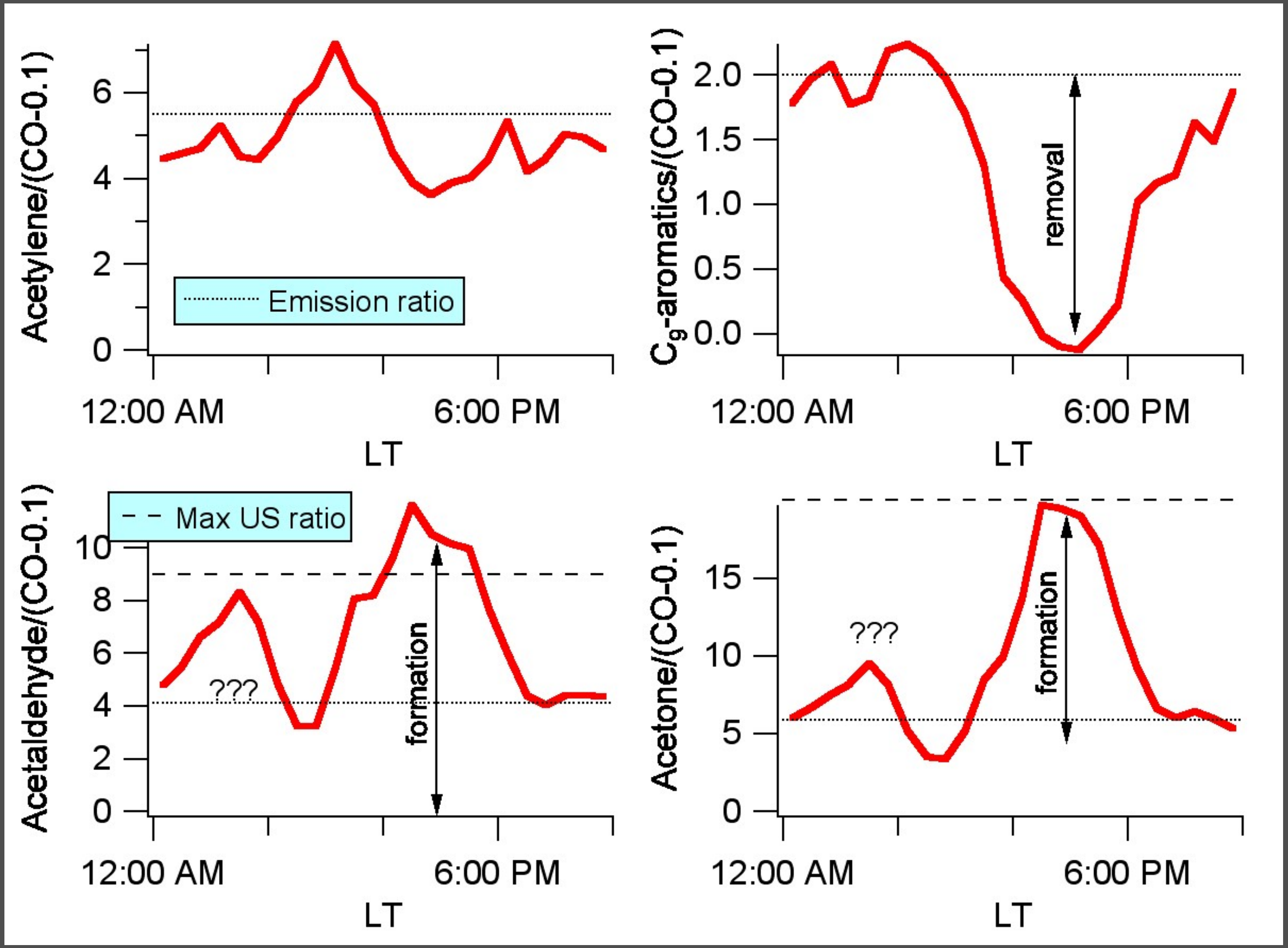
1) Combustion efficiency?

2) LPG – clear signature

	C-130	Warneke et al.*	
Compound	**Urban**	**2004 NE**	**LA**
HCN	0.6		
Formaldehyde	16.0		
Acetaldehyde	15.5	0.7	9.7
Methanol	31.0	4.0	8.4
i-Butane	4.9	1.0	2.6
Butane	14.9	1.7	5.4
i-Pentane	4.5	4.0	6.3
Pentane	3.3	1.6	3.0
Ethanol	10.5	5.8	
Propanal	3.6	0.7	
Acetone	12.8	2.9	14.2
Acetonitrile	0.3		
Butanal	1.3		
MEK	4.3	0.8	1.5
MTBE	3.2		
Benzene	1.2	0.6	1.1
Toluene	6.2	2.6	3.5
Ethyl_benzene	1.2	0.3	

* *Warneke et al., JGR, accepted*

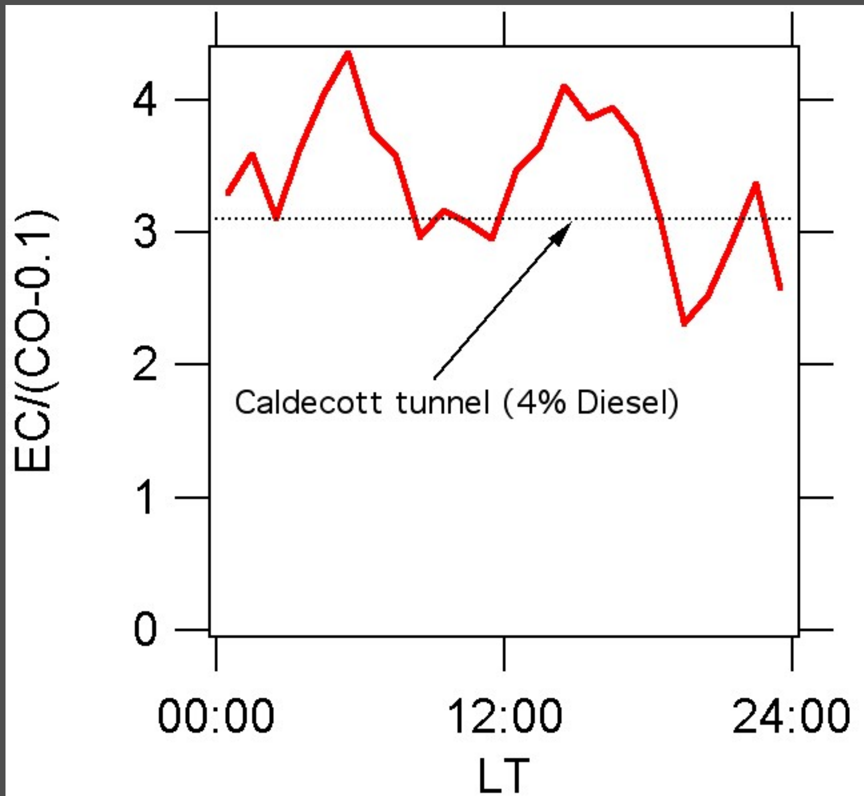
Photo-Chemical Formation of Oxygenated VOCs

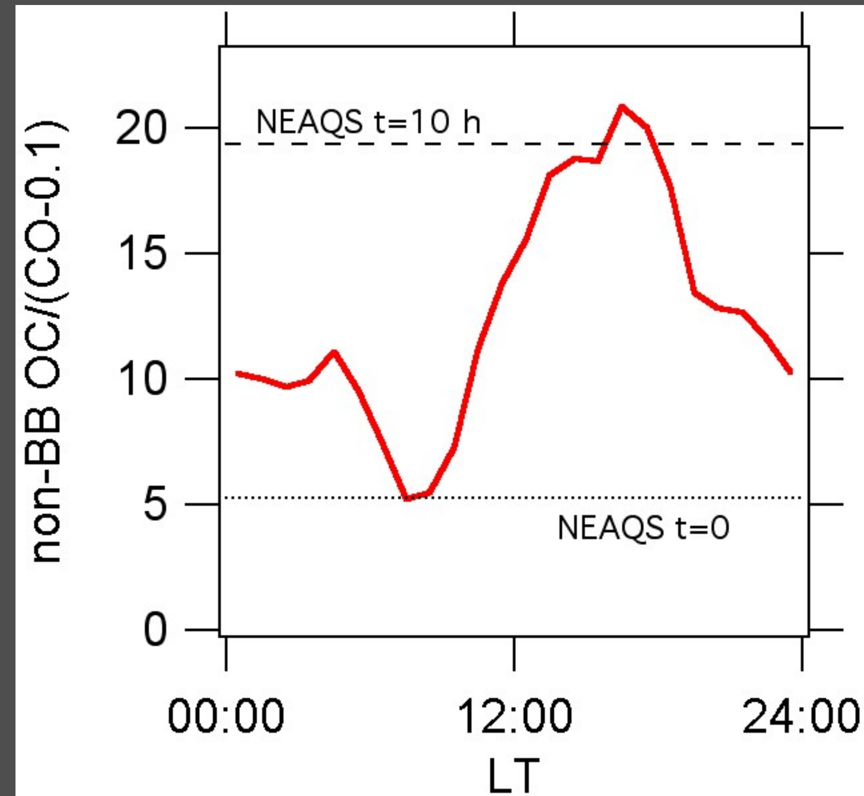


- Emission ratios of most VOCs vs. CO higher than in U.S.
- Secondary acetaldehyde and acetone comparable to U.S.
- Formation not complete at T1?

Data from T1: de Gouw

Diurnal Variation of EC and non-BB OC





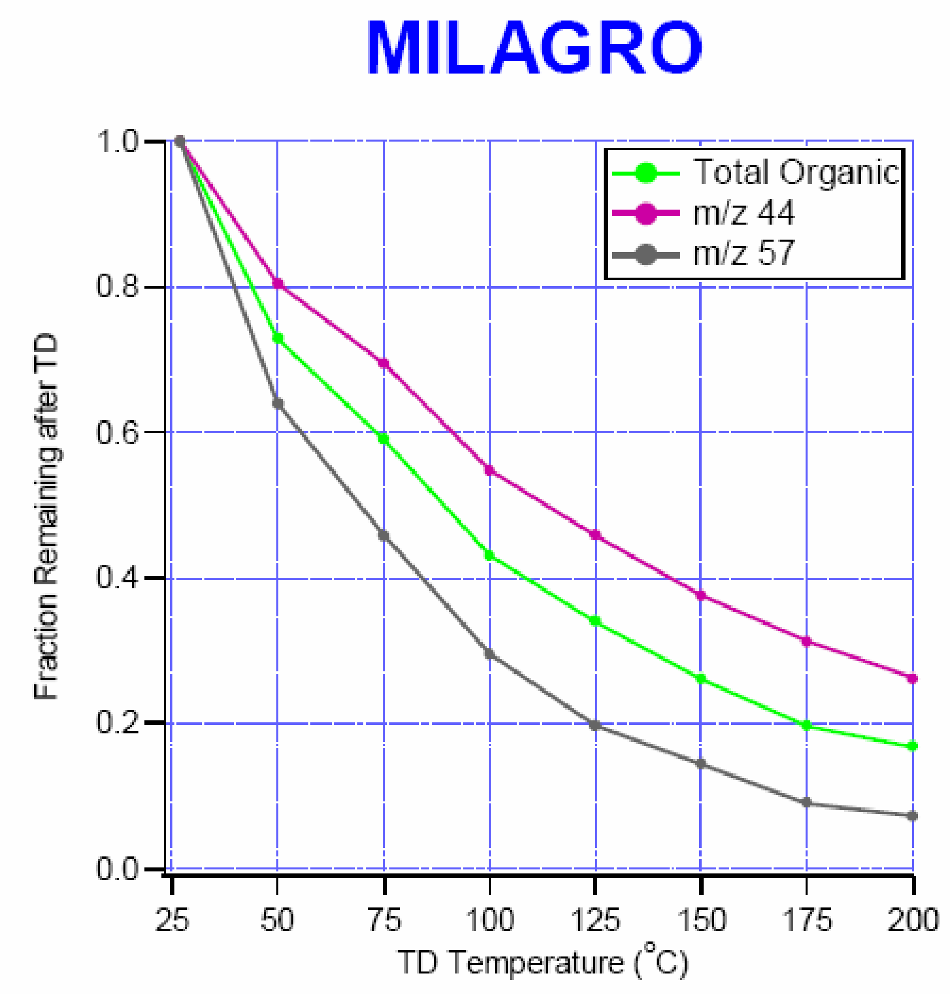
Caldecott data: Kirchstetter 1999

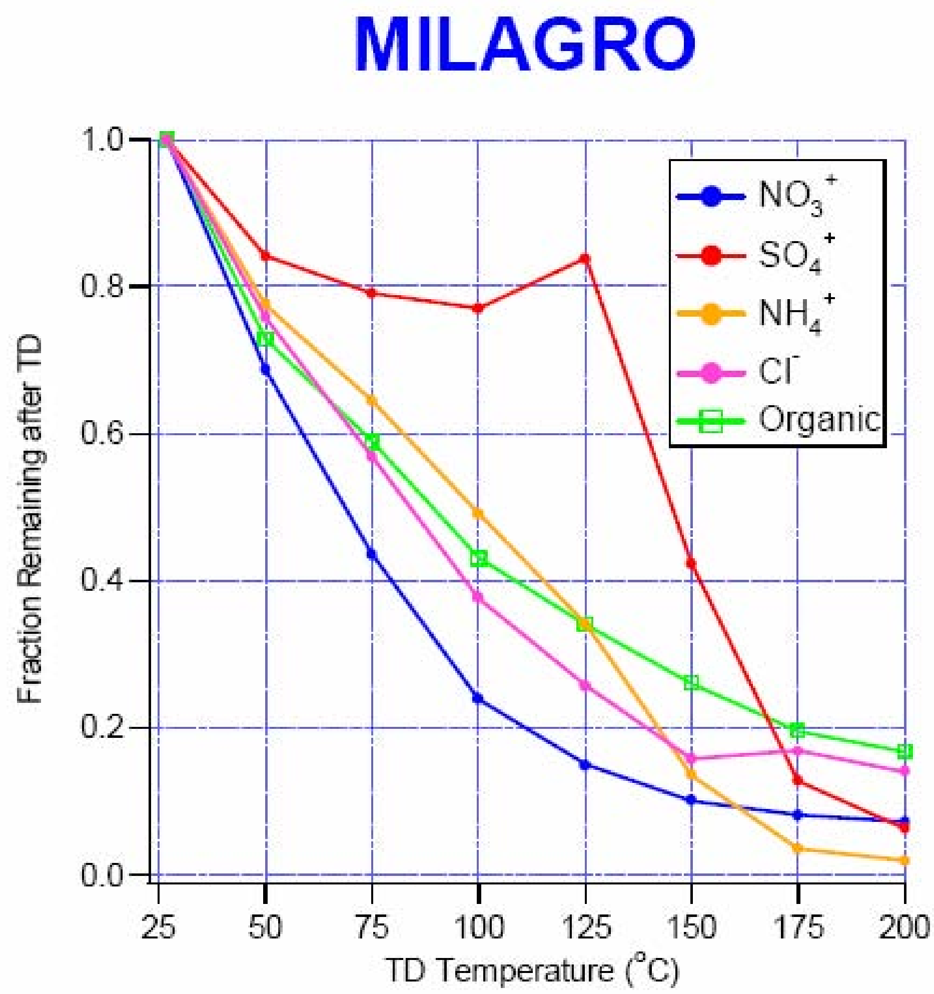
- Secondary formation of OC similar to U.S.
- EC/CO ratio constant ⇒ EC lifetime > 1 day
- EC/CO ratio constant ⇒ mix of vehicles constant

Data from T1: de Gouw

Data from T0: Huffman and Jimenez

- If nitrate evaporates, does urban and fire POA do the same?

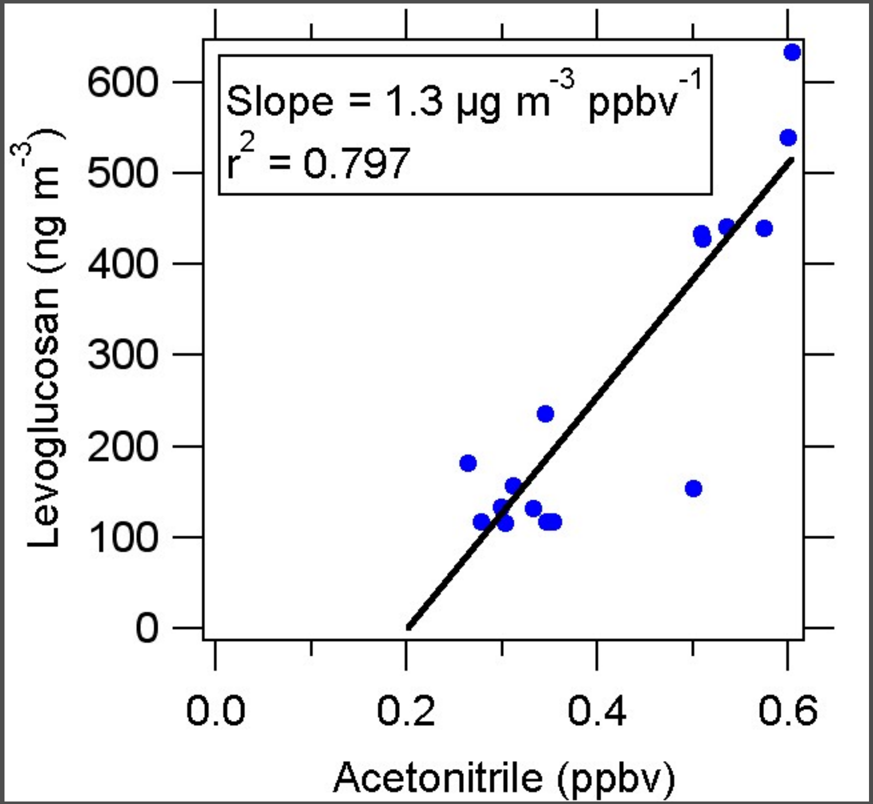


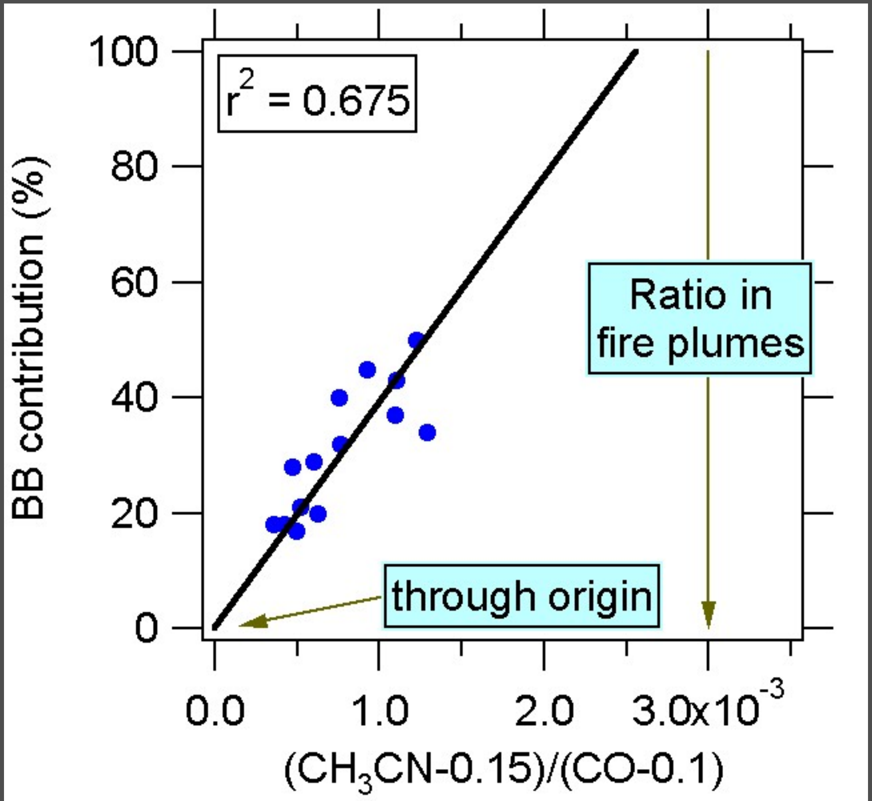


Biomass Burning

- Many methods give insight into relative importance of biomass burning $\Rightarrow$ results need to be carefully examined and compared against each other
- Biomass burning = forest or agricultural fires outside city + urban bio-fuel use
- No method distinguishes between the two
- Diurnal variations can give some insight
- Other concerns: nitriles from vehicles?

Acetonitrile versus Levoglucosan



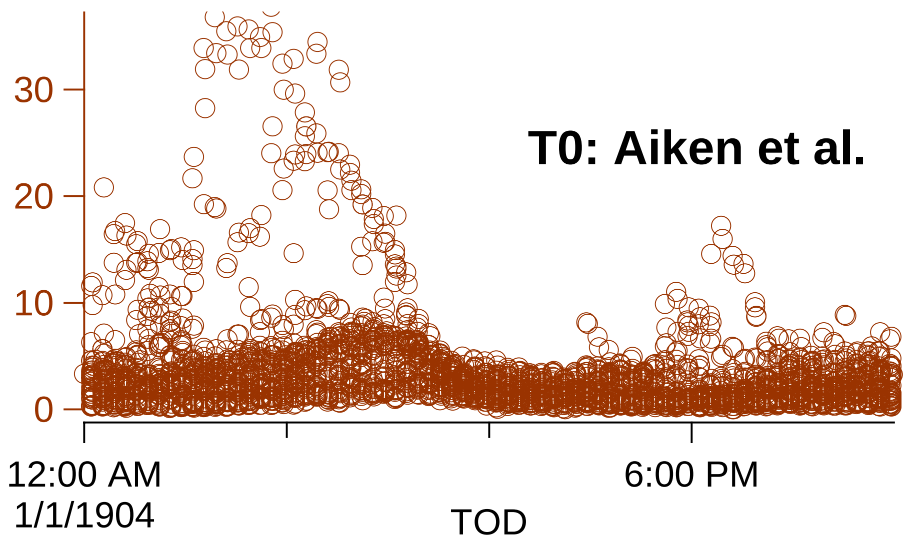


Levoglucosan: Schauer et al.

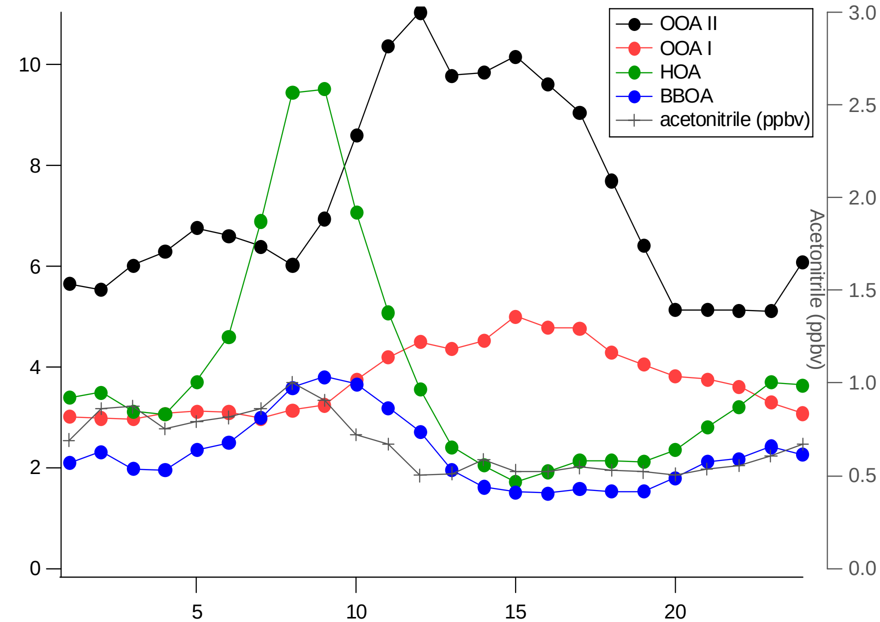
- Acetonitrile correlates with levoglucosan
- CH_3CN/CO ratio correlates with BB contribution estimated using Chemical Mass Balance [*Schauer et al*., in prep.]

Data from T1: Schauer, de Gouw

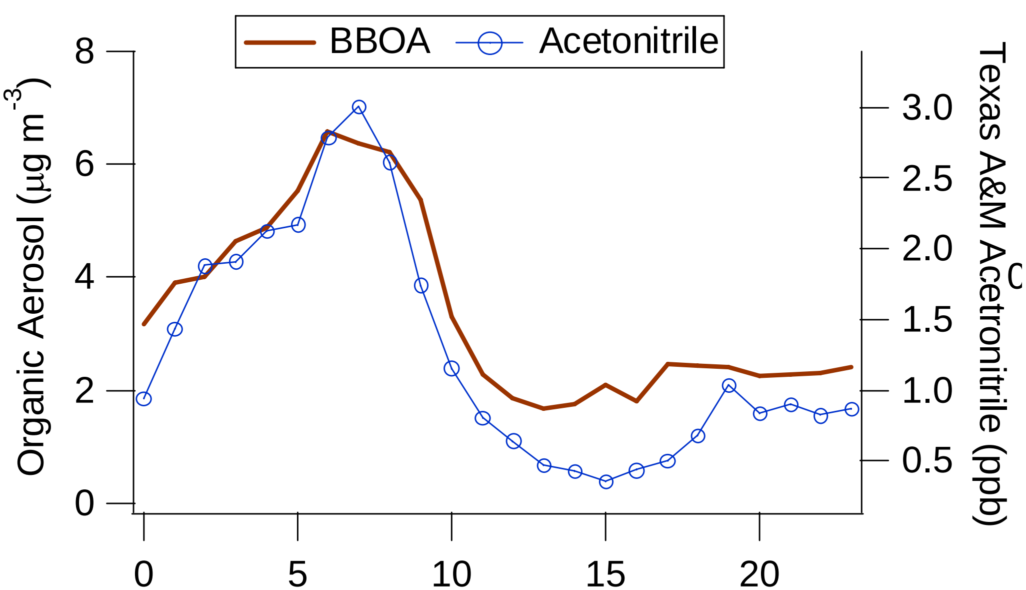
Diurnal cycles of Acetonitrile and BBOA



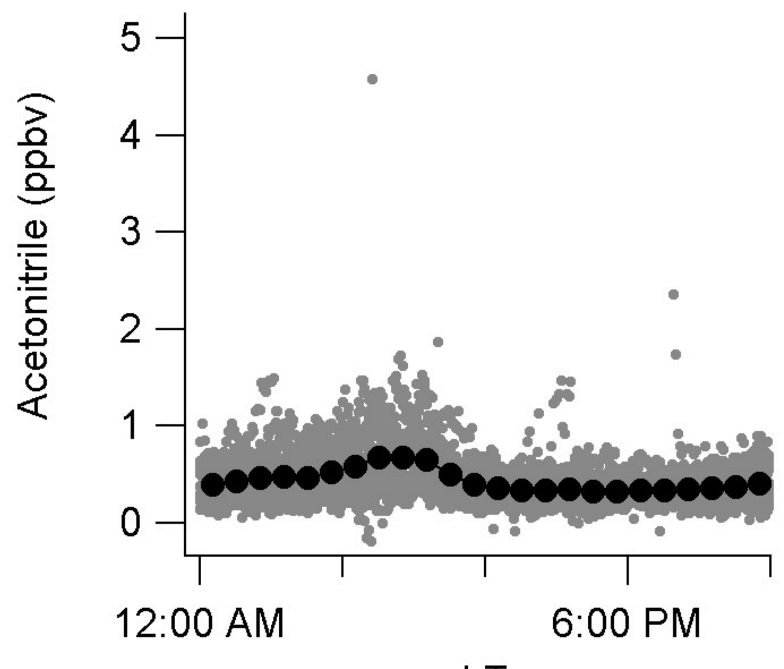
2003: CENICA Supersite



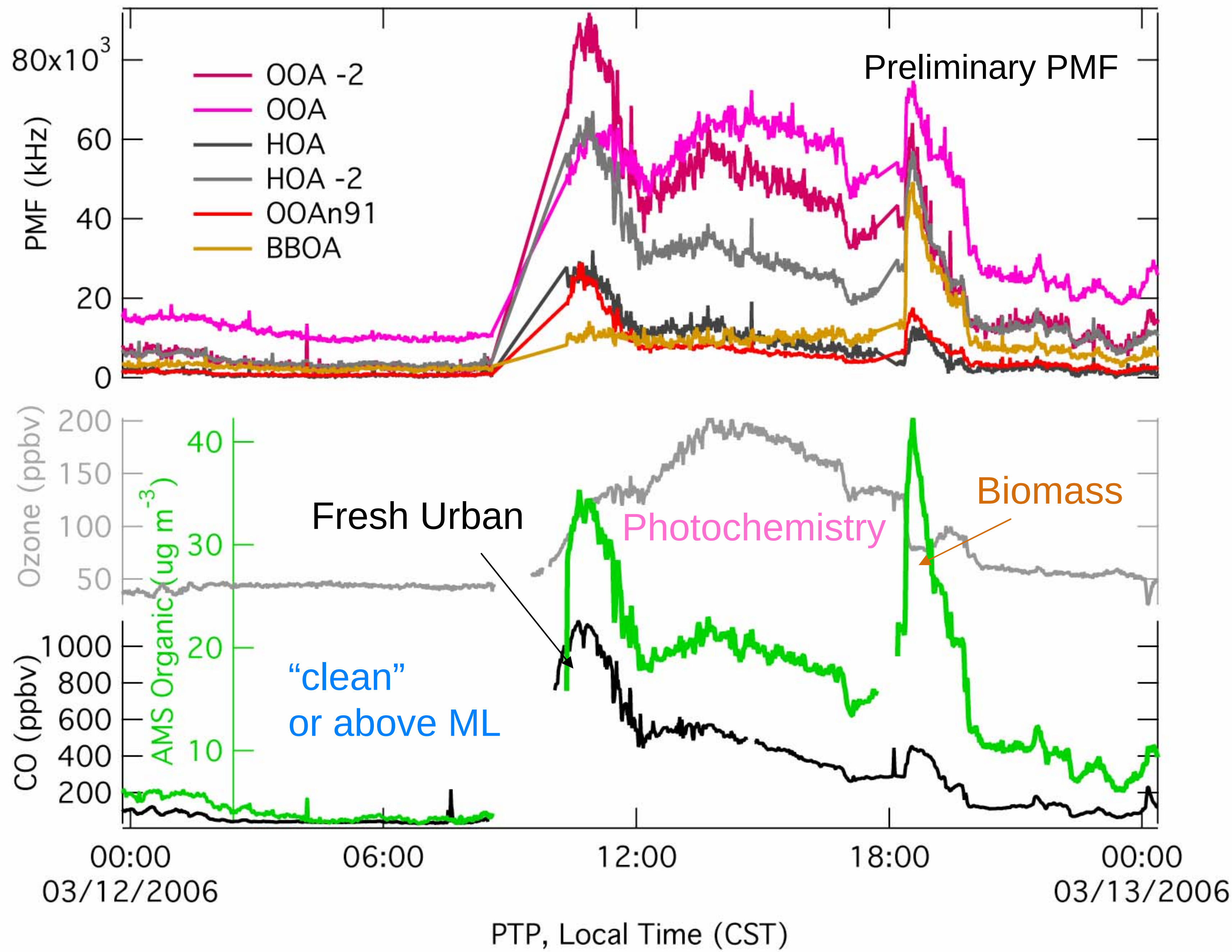
T0: Aiken, RY Zhang et al.



T1: de Gouw, Welsh-Bon et al.



Data from PTP: Herndon



Compare to ground measurements

Data from C130: Apel

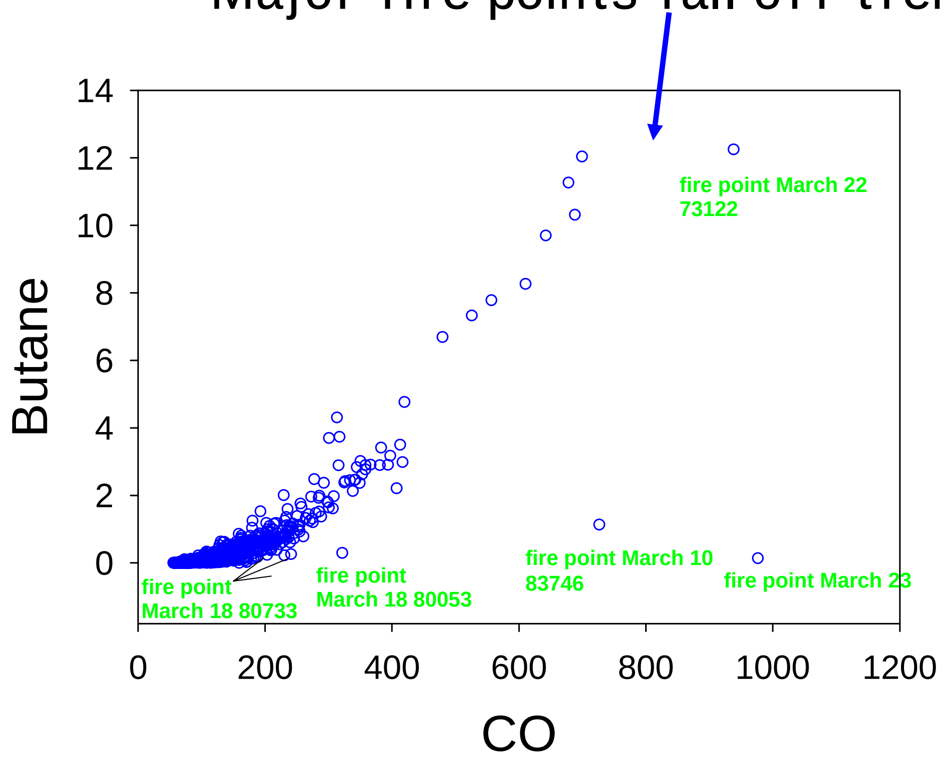
Butane/isobutane 0.33 (Velasco)/0.36 (TOGA)

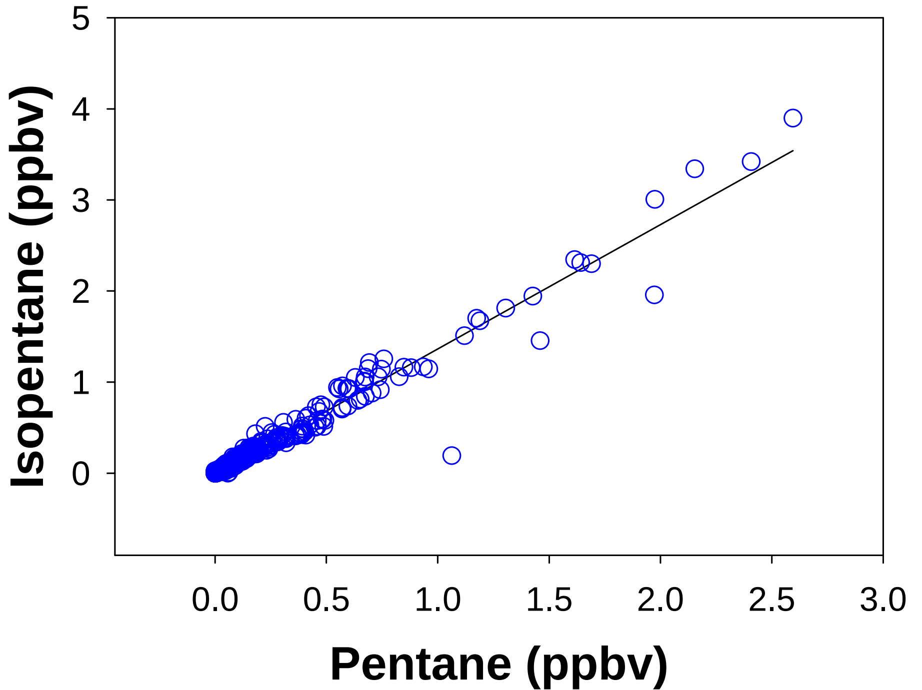
Isopentane/pentane 2.0 (Velasco)/1.4 (TOGA – bottom right)

Toluene/benzene (fresh): 5 (Velasco)/5(TOGA)

Using emission ratios to look at some data

Major fire points fall off trendline – very different ERs

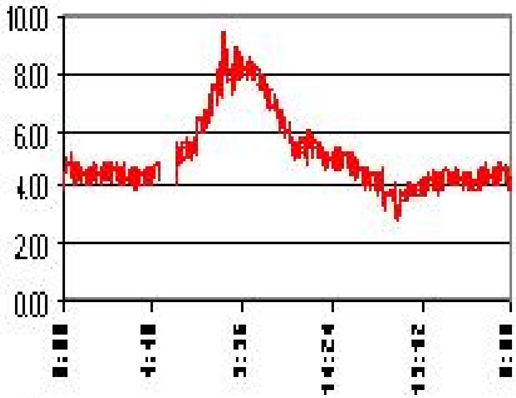


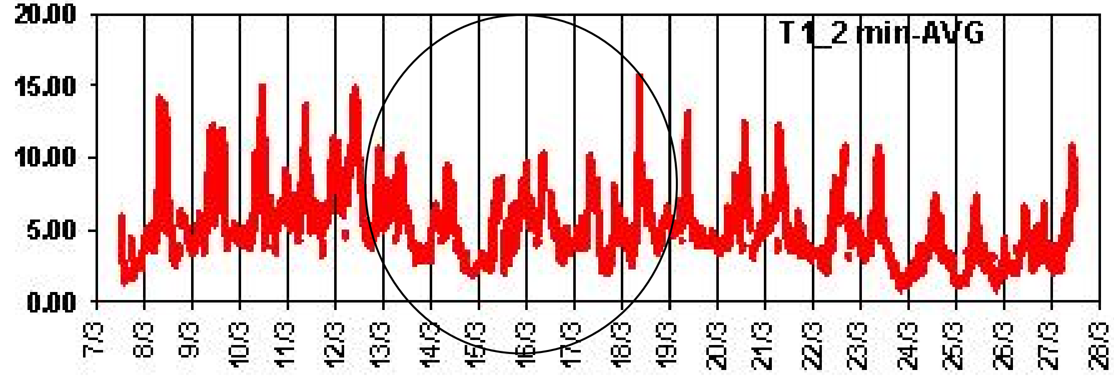


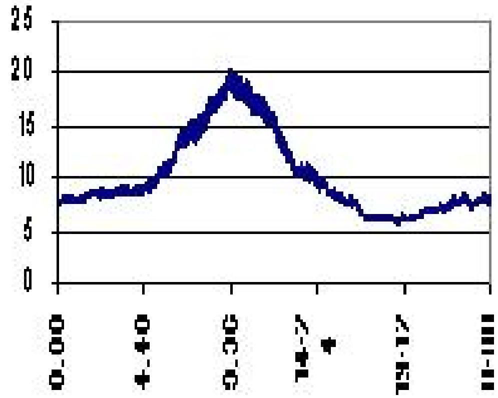
Regional Influences

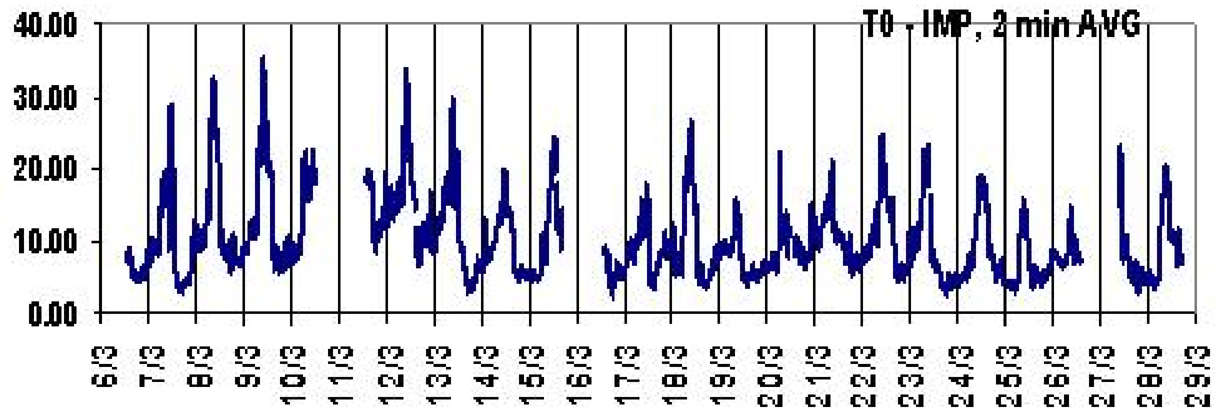
- Air getting into Mexico City not always clean
- Formaldehyde several ppb upwind
- Emissions from Tula
- Volcanic emissions

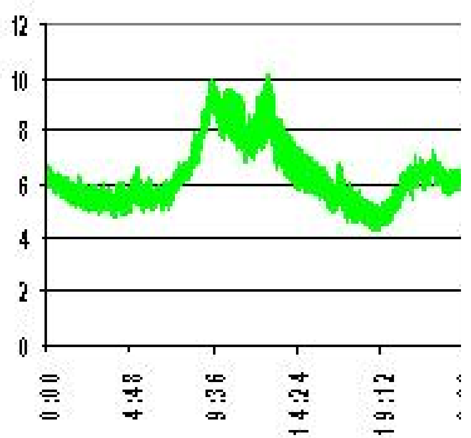
HCHO –Measurements at T-1, T0 and T1, W.Junkermann, FZK IMK-IFU

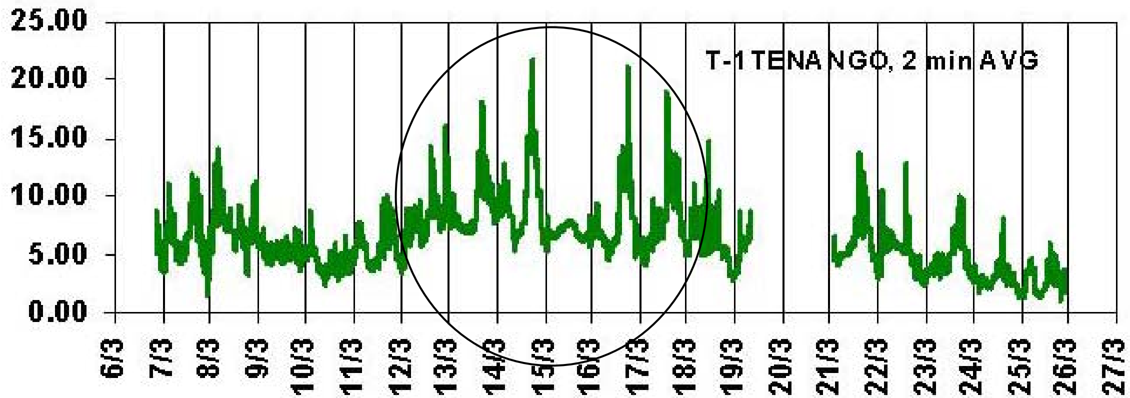










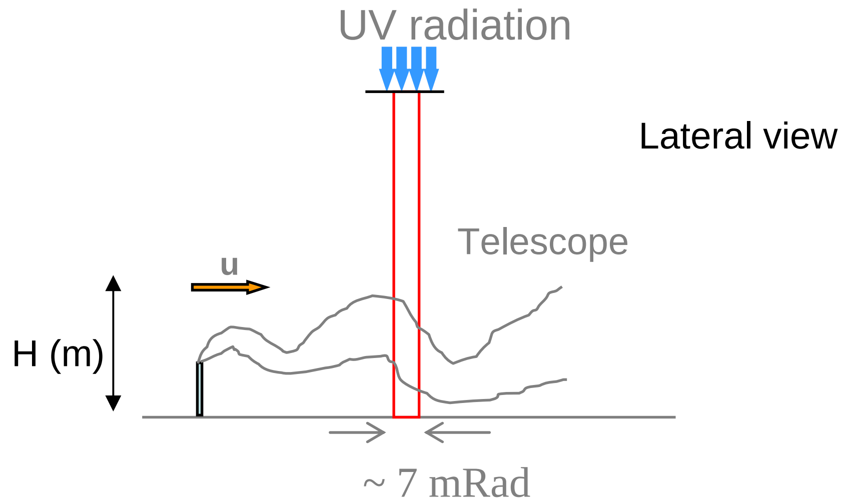


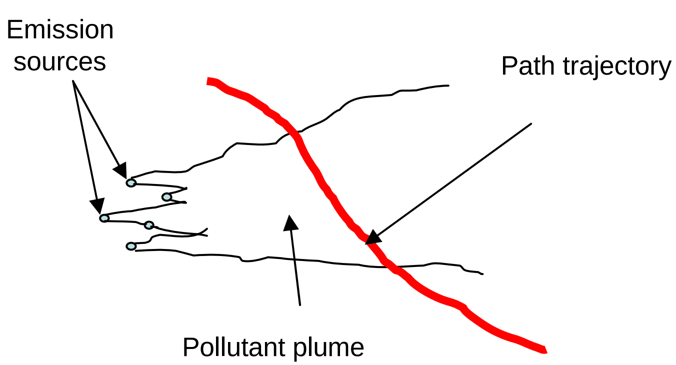
Slide from Michel Grutter

Tula's Industrial Complex

Data from Gustavo Sosa

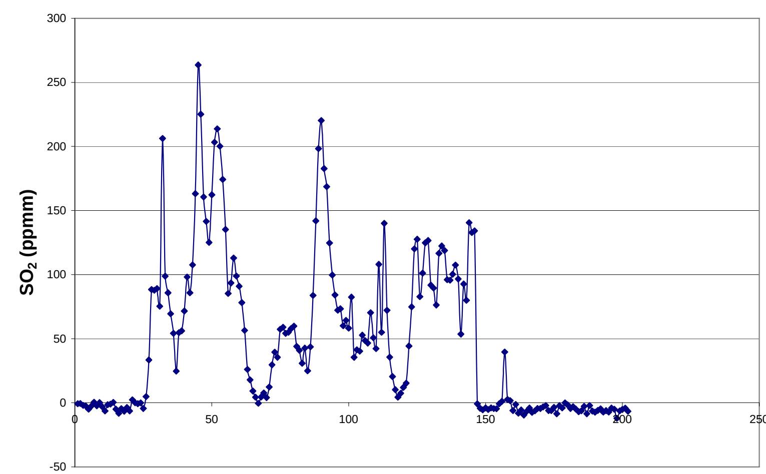
Column Integrated SO_2 concentration Mini-DOAS system





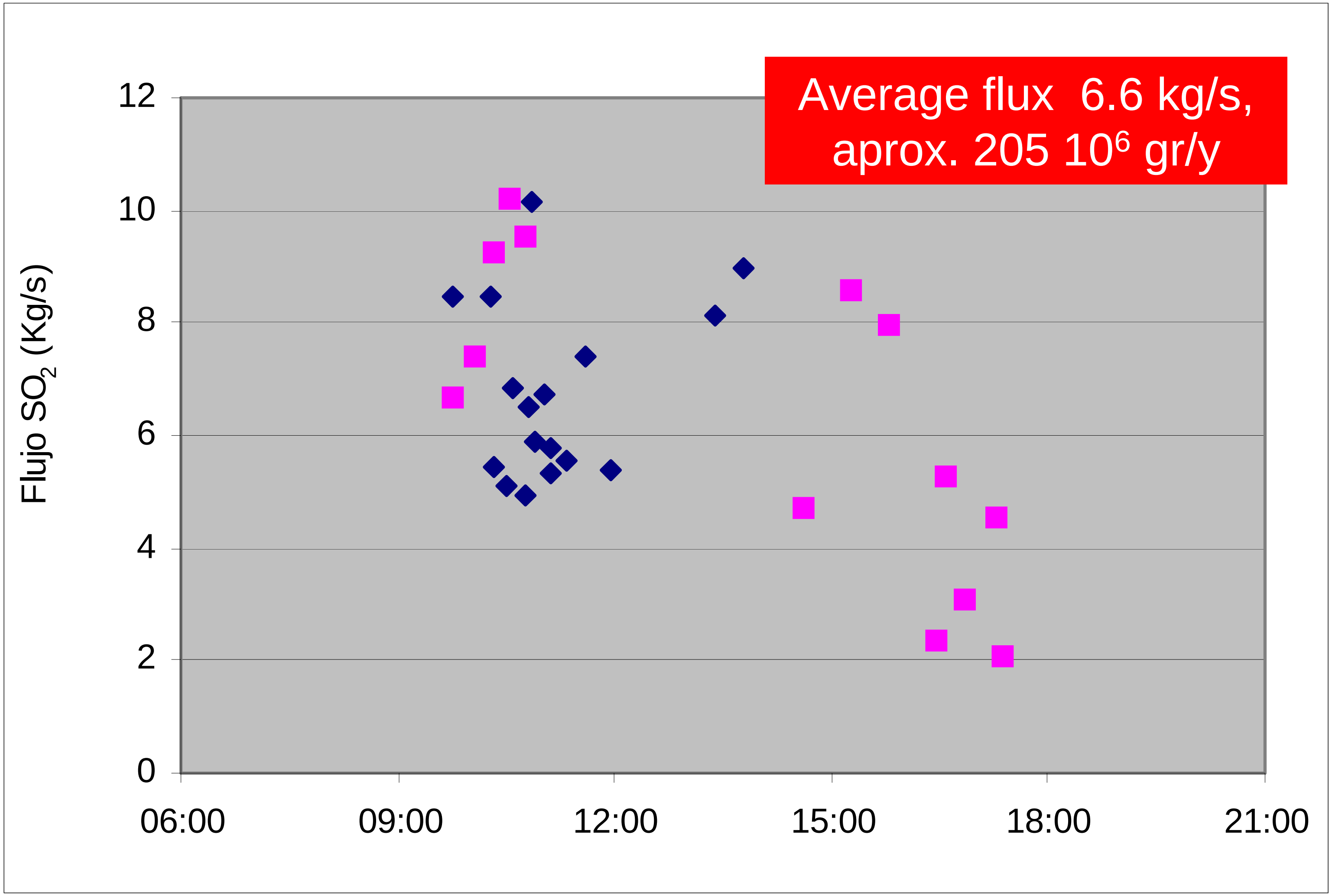
View from above

Transversal plume concentration

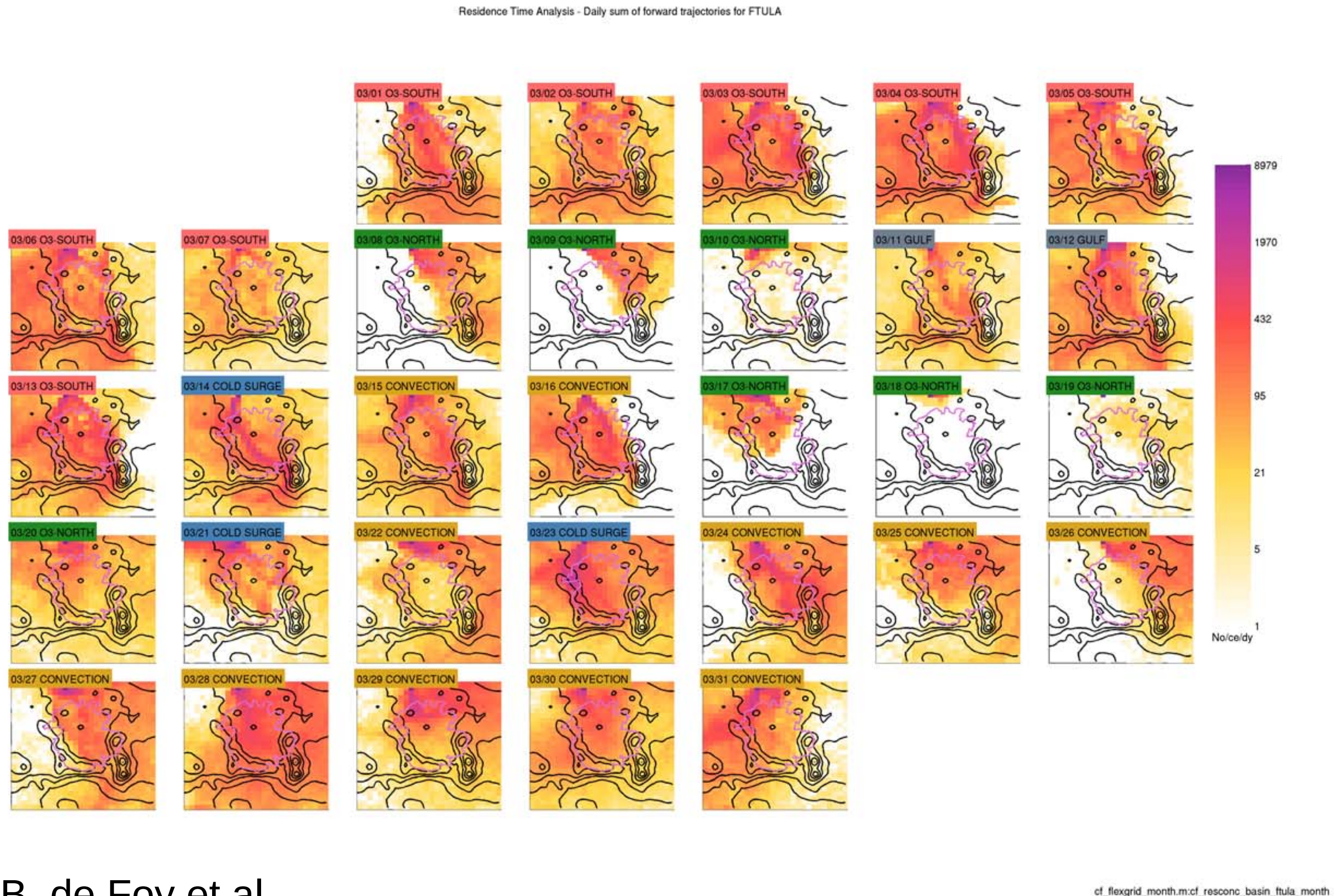


Data from Gustavo Sosa

SO_2 flux emission (kg/s) at Tula industrial area



Residence Time analysis: Daily sum of all forward trajectories from Tula

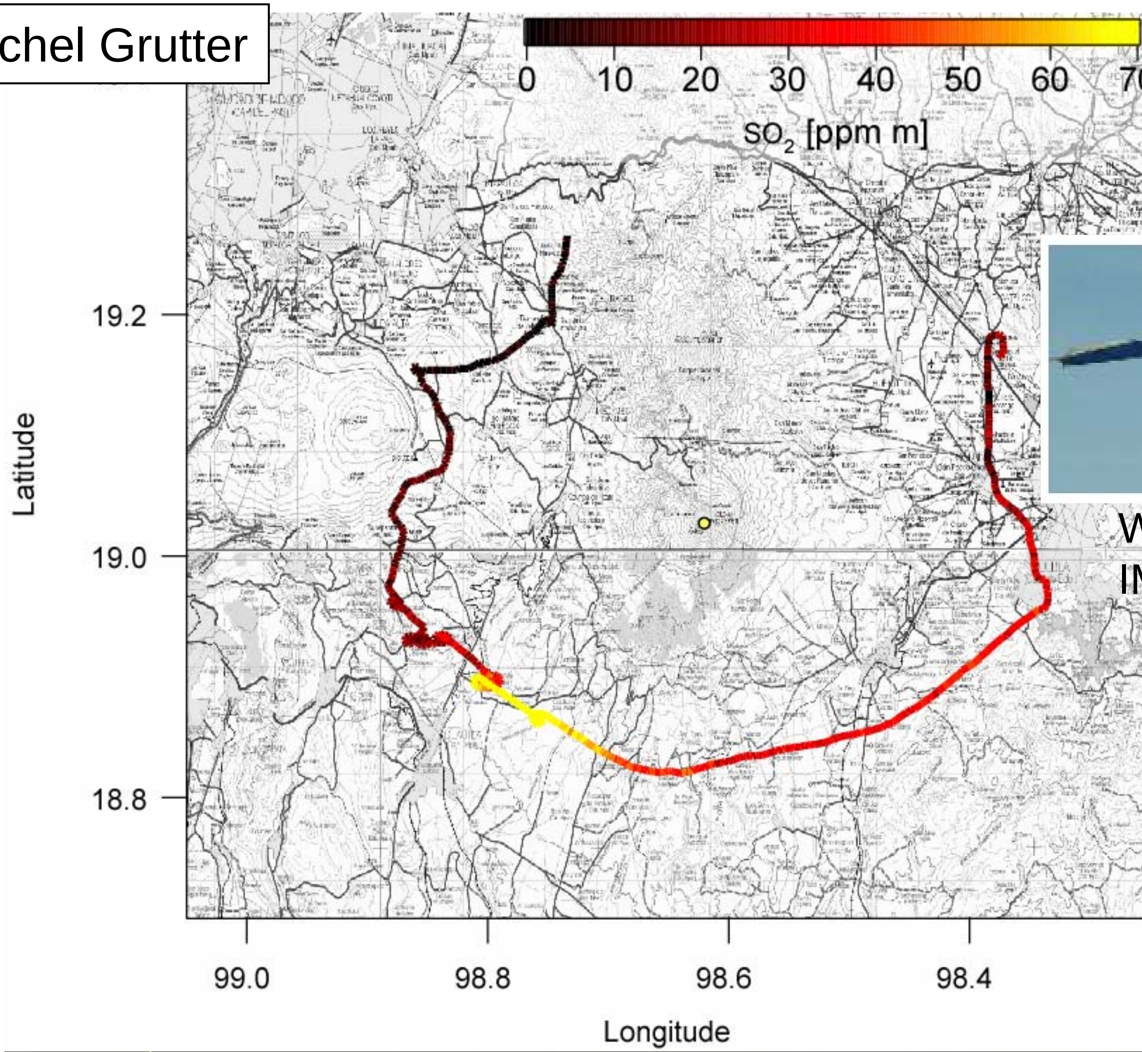


from B. de Foy et al

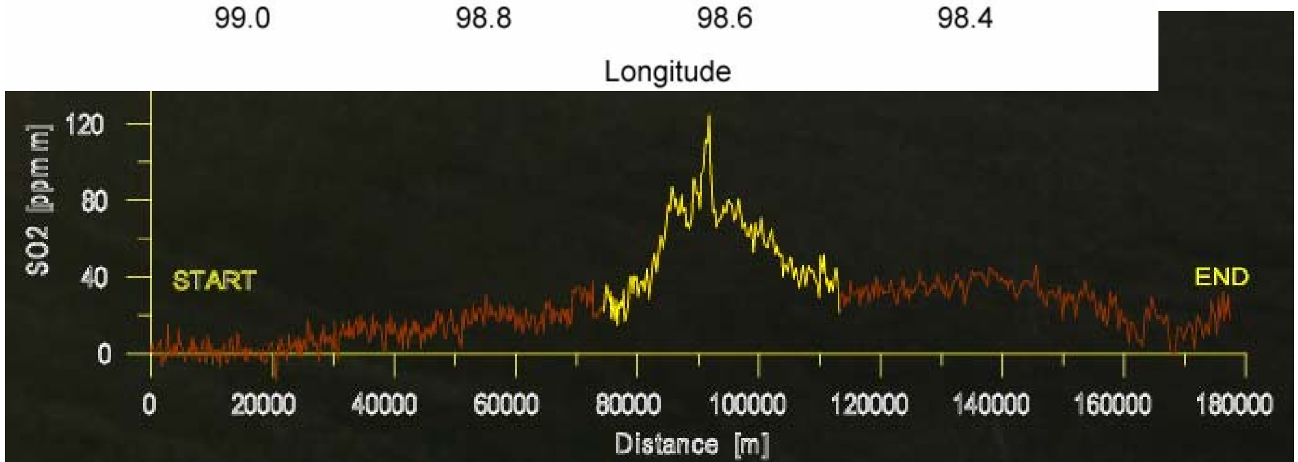
Slide from Michel Grutter

Popocatépetl Volcano

Slide from Michel Grutter



Wolfgang Junkerman
IMK-IFU



Slide from Michel Grutter

SO2 flux measurements were made using a COSPEC mounted in a car and driven under the gas plume coming out from the volcano. The estimates of the SO2 flux are listed in the table below

CENAPRED

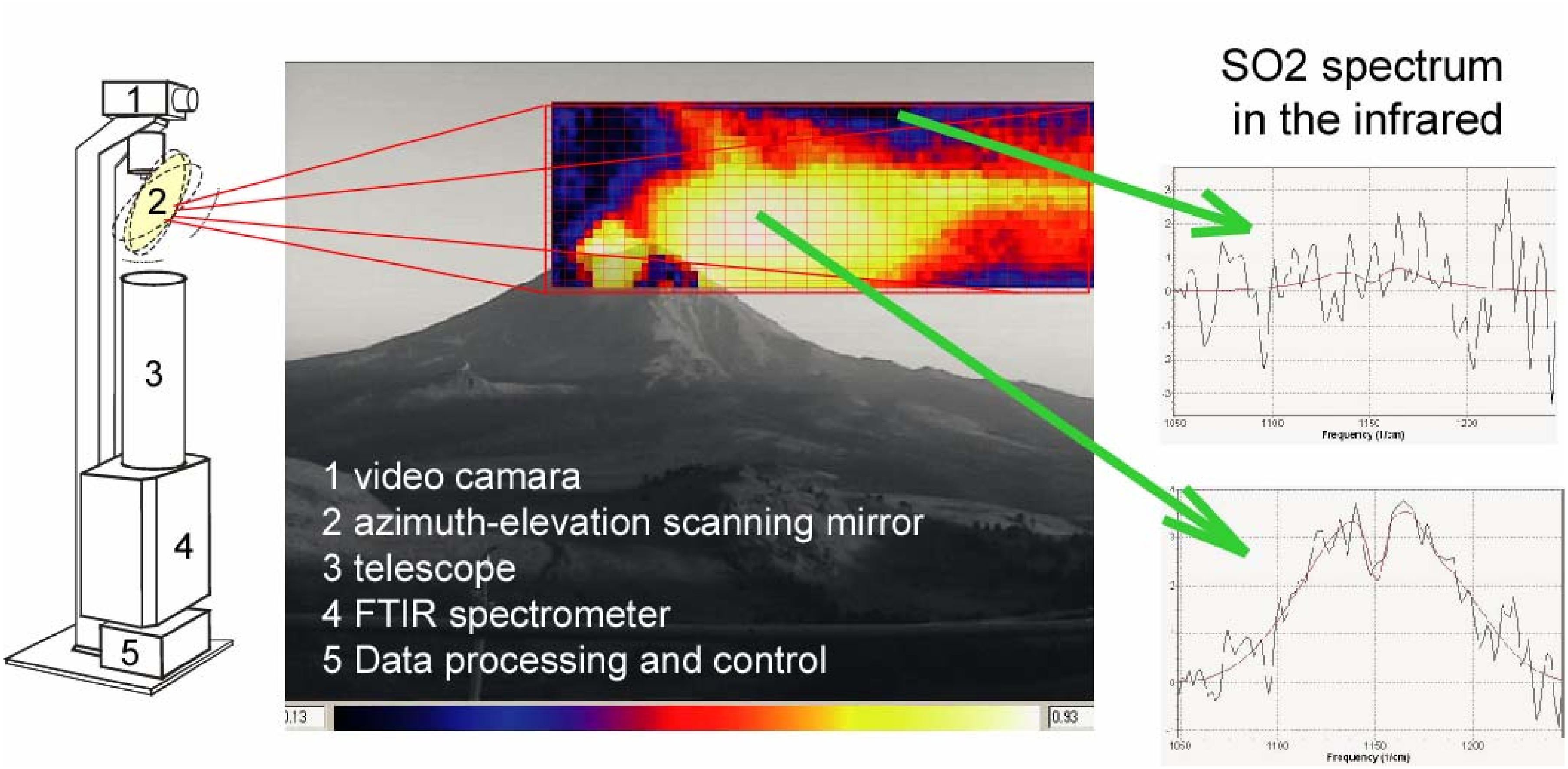
geOFISICA UNAM

Table: SO2 flux measurements from COSPEC

Date	number of scans	wind speed (m/s)	plume altitude (m)	plume width (m)	core width (m)	SO2 flux total	std. dev. total
24-Jan-06	2	5	5900	52439	52439	2114	528
9-Feb-06	4	6	6000	51478	51478	3478	1090
21-Feb-06	3	8	5900	52270	52270	2994	341
9-Mar-06	4	12	5800	34878	34878	2535	668
23-Mar-06	3	15	5500	48368	48368	4982	227
6-Apr-06	2	5	6100	54547	54547	5046	1559
18-Apr-06	3	5	5800	58911	58911	2433	1248

Slide from Michel Grutter

SO_2 plume animation



Papers

- Yes, there will be papers
- We were not brave enough to update previous lists
- Size of the study requires communication across platforms and data sets to come up with a consistent picture
- Much of this work in the early stages and future meetings could be essential